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Factors in the Determination of Selected Trace Elements in Near-Shore U. S. Waters of Lakes Superior and Huron

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16. ABSTRACT

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FACTORS IN THE DETERMINATION OF SELECTED TRACE ELEMENTS IN NEAR-SHORE U.S. WATERS OF LAKES SUPERIOR AND HURON

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ABSTRACT. *Determinations of total As, Cr, Cu, Fe, Mn, and Pb in acidified unfiltered water samples from 48 stations representing the near-shore U.S. waters of Lake Superior, Lake Huron, and selected incoming streams gave overall mean concentrations and standard deviations (μg/L) of 1.0 ± 0.7, 0.9 ± 1.8, 2.0 ± 1.8, 236 ± 819, 14 ± 34, and 0.7 ± 0.8, respectively, using flameless atomic absorption analytical methods. Total concentrations of Ni and Hg were usually less than the instrumental detection limits (μg/L) of 0.8 and 0.02, respectively. Small losses of Hg, As, and Cr from solutions are possible in addition to a molecular spectral interference in the determination of As using the graphite furnace method. River waters usually were only slightly higher in total element concentrations than lake waters, except for Fe and Mn. Nearshore waters of both lakes were very similar in elemental composition.*

INTRODUCTION

The importance of trace elements as related to aquatic life productivity, toxicity, accumulation and transport in the aquatic environment has been expressed in many investigations. In spite of this, relatively few published reports deal specifically with baseline trace element concentrations for some of the world's largest freshwater lakes, namely Lakes Superior and Huron (Weiler and Chawla 1969; Chau and Saitoh 1973; Wagner *et al.* 1976; Glass and Poldoski 1976). With inevitable future pressures for increases in industrial activities and energy production, it is imperative that reasonably accurate baselines be established.

This study is an attempt to determine the applicability of certain analytical procedures and to help provide information on baseline concentrations of As, Cr, Cu, Fe, Mn, Ni, Pb, and Hg in selected near-shore U.S. Waters of Lakes Superior, Huron, and incoming streams. Results generally focus on concentration differences between near-shore waters and corresponding waters such as harbors and river mouths for a single time period.

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EXPERIMENTAL

Sampling

During the months of June and July 1975 the Michigan Department of Natural Resources, in cooperation with the U.S. Environmental Protection Agency and the U.S.-Canadian International Joint Commission, sampled Lakes Superior and Huron near-shore waters and the mouths of incoming streams for several trace elements. The general scheme was that each locale was comprised of a pair: a station off-shore by approximately 2500 meters and another site located either 100 meters off-shore or up into a river mouth. Table 1 gives general locations, station coordinates and sampling depth. Most stations were located in areas of low population density (rural and semirural), although some areas were expected to show evidence of man's activities such as the Saginaw River entering Saginaw Bay, Lake Huron. General water quality characteristics for Lake Superior have been reported (U.S.-Canadian International Joint Commission 1977). All lake stations were sampled at mid-depth in at least triplicate using a one-liter Kemmerer-type sampler which was dropped separately for each replicate sample. For stream sampling, one-

TABLE 1. Location and depth of 1975 sampling stations for Lakes Superior and Huron.

Location	Station Number	Coordinates		Sampling Depth (meters)
		N. Latitude	W. Longitude	
Lake Huron				
Lexington	20-1-	43°16'12"	82°31'10"	2.5
	4-	43°16'27"	82°29'39"	5.5
Harbor Beach	19-1-	43°50'40"	82°38'23"	2.0
	4-	43°50'43"	82°36'27"	7.0
Saginaw Bay	18-R-	43°38'35"	83°50'54"	0.3
	4-	44°07'43"	83°18'45"	11.0
Tawas	17-R-	44°15'32"	83°31'48"	0.5
	4-	44°14'49"	83°29'26"	4.0
Harrisville	16-1-	44°42'40"	83°15'56"	2.5
	4-	44°42'42"	83°14'30"	4.5
Alpena	15-R-	45°03'44"	83°25'40"	0.3
	1-	45°03'18"	83°25'00"	2.5
	4-	45°00'31"	83°21'15"	7.5
Presque Isle	14-1-	45°21'34"	83°32'17"	3.0
	4-	45°22'02"	83°32'02"	15.0
Calcite	22-1-	45°24'40"	83°46'41"	2.5
	4-	45°25'30"	83°45'18"	9.0
Cheboygan	13-R-	45°39'09"	84°28'00"	0.3
	1-	45°39'30"	84°27'41"	4.0
	4-	45°41'20"	84°26'02"	7.0
DeTour	12-1-	45°57'06"	83°55'07"	3.5
	4-	45°56'20"	83°55'07"	12.0
Lake Superior				
Tahquamenon River	25-R-	46°33'30"	85°01'53"	0.3
	4-	46°35'00"	84°56'39"	7.5
Grand Marias	10-1-	46°40'48"	86°59'00"	4.5
	4-	46°41'55"	86°59'32"	9.0
Munising	9-R-	46°24'21"	86°38'30"	0.3
	4-	46°27'02"	86°38'08"	15.0
Carp River	21-R-	46°31'08"	87°23'03"	0.3
	4-	46°32'16"	87°20'45"	13.0
Marquette - Harbor Area	24-1-	46°32'30"	87°22'55"	4.5
	4-	46°31'30"	87°22'14"	7.5
Presque Isle	8-R-	46°34'38"	87°23'33"	0.3
	4-	46°33'49"	87°21'22"	15.0
Lower Portage	4-R-	46°58'55"	88°26'07"	0.3
	4-	46°57'23"	88°24'15"	15.0
Upper Portage	3-R-	47°14'06"	88°37'45"	0.3
	4-	47°16'45"	88°39'00"	13.0
Big Bay	7-1-	46°50'00"	87°43'20"	4.5
	4-	46°51'15"	87°42'24"	15.0
Eagle Harbor	5-1-	47°27'50"	88°08'37"	5.0
	4-	47°28'15"	88°08'33"	15.0
Isle Royale	6-2-	47°56'20"	88°46'30"	15.0
	5-	48°03'20"	88°49'53"	15.0
Ontonagon	2-R-	46°52'37"	89°19'40"	0.3
	4-	46°54'45"	89°21'45"	15.0
Black River	1-R-	46°40'00"	90°02'52"	0.3
	4-	46°41'40"	90°04'08"	15.0

liter sample storage bottles were dipped 0.3 m below the surface of the water in the river mouth sufficiently upstream to avoid influence from lake waters.

Sample containers, constructed of either polyethylene (plax) or FEP teflon® (Nalgene),[2] were precleaned by rinsing them with 1:1 HNO_3 and then deionized distilled water. They were subsequently leached with 0.2% v/v nitric acid for about 2 weeks or longer prior to sample collection. Three one-liter polyethylene bottles were filled at each station (A, B, C) after rinsing each bottle with a water sample. At selected stations, two additional samples were subsequently taken in teflon (D, E). Two milliliters of nitric acid (Mallinkrodt reagent grade) were added to each of the B and D samples in the field, constituting a 0.2% v/v concentration. Samples were labeled, placed in plastic bags, packed in ice, and shipped in a sealed cooler chest to arrive at the laboratory approximately 2 days after sample collection.

Sample Handling, Filtration, and Blanks

Shortly after arrival at the laboratory, the C and E samples of each station were filtered. Filtered samples and the A, C, and E unfiltered samples to which acid had not been added in the field were immediately preserved with nitric acid. All samples were stored under near dark conditions at 4°C. For Hg analyses, the unfiltered B and D samples were subsampled usually within 2-3 days after collection into decontaminated pyrex reaction flasks along with analytical reagents (H_2SO_4, HNO_3, $KMnO_4$) as employed in the flameless cold vapor analytical method subsequently described. The filtration apparatus (Millipore aseptic filtration unit) was equipped with a 0.1 μm pore size membrane filter (Millipore). Before each filtration the apparatus was cleaned by rinsing it with 10% v/v nitric acid and then liberally with deionized distilled water. A new filter was installed for each sample and it was rinsed with 200-mL of 0.2% nitric acid followed by a 200-mL rinse with deionized distilled water. The last portion of water (50-mL) was collected directly into a 60-mL cleaned polyethylene storage bottle (Nalgene), which was placed within the receiver of the filtering unit. This portion was acidified and served as an individual blank for each corresponding filtered sample. A 100-mL aliquot of the lake or river sample was subsequently filtered, discarding the first 50-mL and collecting the last 50-mL directly in a similar storage container.

Several of the one-liter polyethylene sample storage bottles containing 0.2% v/v nitric acid were shipped regularly to the laboratory with the samples and they served as blank containers. Shortly after arrival, they were emptied, rinsed with deionized distilled water, and refilled with 0.2% v/v nitric acid. These solutions were analyzed during the routine analysis of lake samples.

The one-liter Kemmerer sampler was cleaned by washing with dilute acid and rinsing with deionized distilled water before sampling began. It was shipped to the laboratory at the conclusion of the lake sampling to check for possible contamination by rinsing the inside of the sampler four times with one-liter volumes of deionized distilled water and after a 5-min residence time, the fourth rinse was placed in a precleaned one-liter teflon bottle. This was acidified and analyzed (subsequently discussed).

Selected samples were pressure digested using hydrofluoric acid as previously described (Poldoski 1977).

Instrumental Methods of Analysis

All analyses were made using atomic absorption spectrometry and instrumentation (Perkin Elmer) included a Model 305B atomic absorption spectrophotometer with an HGA-2100 graphite furnace and a Model 403 with a HGA-2000 graphite furnace, each equipped with a Model 56 recorder. All reagents were of analytical reagent grade quality or better. Table 2 summarizes typical instrumental operating conditions and trace element analyses were generally performed according to that previously outlined (Poldoski and Glass 1977). Simultaneous deuterium arc (D_2) background correction was routinely employed except in the Hg and Cr determinations. An electrodeless discharge lamp was used for As determinations. Analyses of Cu, Pb, Ni, Mn, Fe, Cr and As were made using graphite furnace atomization however, abnormally high concentrations of Mn and Fe were measured with conventional flame techniques (Perkin Elmer Corp. 1971) using the Model 403 spectrophotometer with an air-acetylene flame. Total Hg was determined with the Model 403 using the flameless cold vapor technique (Hatch and Ott 1968) with persulfate digestion (Kopp *et al.* 1972), which was slightly modified (Olson *et al.* 1975) to achieve a lower detection limit. Standardization of all methods was made by the method of additions usually to at least one of the samples per station

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[2] mention of trade names or commercial products does not constitute endorsement or recommendation for use.

TABLE 2. Typical operating conditions and characteristics for furnace atomic absorption analysis of lake and river samples.

	As	Cr	Cu	Fe	Mn	Ni	Pb
Wavelength (nm)	193.7	357.9	324.7	248.3	279.5	232.0	283.3
Atomization[a] temperature-time setting (°C/sec)	2,800/8	2,700/8	2,700/6	2,600/8	2,500/8	2,800/8	2,550/6
Charring temperature-time setting (°C/sec)	175/25	1,200/15	1,000/15	1,200/15	1,000/15	1,200/15	500/20
Working detection limit[b] (μg/L)	0.2	0.3	0.2	0.4	0.05	0.8	0.2
Mean percent recovery	104 ± 7[c]	84 ± 13	101±10	95 ± 23	104 ± 11	92 ± 11	85 ± 15

[a]Based on temperature scale calibrated for 225 amps passing through HGA-2100 furnace at 50 scale divisions.
[b]Operationally defined as concentration corresponding to peak height equivalent to 2X width of normal baseline fluctuations.
[c]± - Indicates standard deviation of mean (this designation also applies in the following tables).

except for mercury determinations. Frequent use of standard additions for determining mercury was not normally required. The concentrations of other samples from a station were calculated based on the determined percent recovery factor for that station. To assure that standards were prepared accurately, quality control standards for water issued by the U.S. Environmental Protection Agency, EMSL-Cincinnati, were analyzed. Mean values (measured concentration/stated concentration) obtained were: As = 1.04; Cr = 0.98; Cu = 1.03; Fe = 0.98; Hg = 0.86; Mn = 1.00; and Pb = 1.07.

RESULTS AND DISCUSSION

Sample Handling

The effects from contamination, solution stability, and resultant overall reproducibility were of major concern. Therefore, the employed procedures were designed to provide various internal checks from sampling through analysis. A high quality of deionized distilled water (Millipore, Super Q System) was employed which provided an analytical baseline. Table 3 lists measurements of the various types of contamination checks which were performed. From storage of blank 1 (blank 2), it is seen that some contamination is evident; significant concentrations of Hg and Mn are present. Particularly noticeable is the mean blank value for Hg, which was above most sample concentrations. The reason for this result was not ascertained since most of the measured sample concentrations were near or below the analytical method's detection limit of 0.02 μg/L. Previous work (Bothner and Robertson 1975) suggested that contamination of solutions may occur via permeation of Hg through polyethylene. However, this was not a logical explanation in this case since samples and blanks were stored under similar conditions. For Mn, blank 2 was subtracted from all unfiltered samples stored in polyethylene.

Another source of possible contamination was from the water sampler as indicated by blank 4. Cu was the only observed contaminant and this value was subtracted from all lake samples.

Sample filtration was observed to be the step most subject to contamination as indicated by blank 3. For Cu, Fe, and Mn the occurrence of contamination was most frequent. Therefore, for this study determinations corresponding to the "dissolved" fraction for these elements were limited by this factor.

Sample Stability

Table 4 depicts some results of storing acidified Lake Superior water under conditions used in this study with and without an added standard spike concentration of the element. Nine fresh replicate

TABLE 3. Typical degrees of contamination from various sources.

Blank #	Source	Trace element concentration (μg/L)							
		As	Cr	Cu	Fe	Hg	Mn	Ni	Pb
1	Fresh 0.2% v/v HNO_3	<0.2	<0.3	<0.2	<0.4	<0.02	<0.05	<0.8	<0.2
2	0.2% v/v HNO_3 stored in polyethylene containers used for collection of unfiltered samples	<0.2	<0.3	<0.2	<0.4	0.03 ± 0.01	0.08 ± 0.13	<0.8	<0.2
3	Deionized distilled water passed through Millipore filter and subsequently acidified (filtration blank)	<0.2	<0.3	0.4 ± 0.3	1.6 ± 1.4	—	0.05 ± 0.01	<0.8	<0.2
4	Deionized distilled water rinse from water sampler	<0.2	<0.3	0.4	<0.4	<0.02	<0.05	<0.8	<0.2

TABLE 4. Effect of storage time on trace element concentrations (μg/L) in Lake Superior water samples. Samples were stored acidified (0.2% v/v HNO_3) at 4°C in both polyethylene and teflon containers, maintained under near-dark conditions.

Element	Mean storage time (days)		
	0	40	106
As(V)			
Lake water	0.99 ± 0.05	0.76 ± 0.10	0.79 ± 0.03
Lake water + 4 μg/L	4.97 ± 0.14	4.37 ± 0.27	3.62 ± 0.13
Cr(VI)			
Lake water	0.41 ± 0.01	0.41 ± 0.11	<0.3
Lake water + 1 μg/L	1.43 ± 0.03	1.24 ± 0.08	0.88 ± 0.07
Cu(II)			
Lake water	1.08 ± 0.00	1.21 ± 0.08	1.10 ± 0.03
Lake water + 5 μg/L	6.08 ± 0.09	6.15 ± 0.33	5.94 ± 0.21
Ni(II)			
Lake water	<0.8	<0.8	<0.8
Lake water + 5 μg/L	4.98 ± 0.19	4.94 ± 0.45	5.11 ± 0.55
Pb(II)			
Lake water	0.24 ± 0.10	0.21 ± 0.05	0.29 ± 0.08
Lake water + 1 μg/L	1.19 ± 0.02	1.21 ± 0.07	1.24 ± 0.02
Mn(II)			
Lake water	3.67 ± 0.17	4.10 ± 0.54	4.81 ± 0.24
Lake water + 10 μg/L	14.28 ± 0.16	15.0 ± 1.35	15.08 ± 0.70
Hg(II)			
Lake water	<0.02[a]	<0.02[b]	<0.02[c]
Lake water + 0.09 μg/L	0.08 ± 0.01[a]	0.08 ± 0.01[b]	0.07 ± 0.01[c]

[a]Measurement made after 5 minutes of storage.
[b]Measurement made after 1 day of storage.
[c]Measurement made after 5-6 days of storage. Samples were routinely preserved with 0.2% v/v HNO_3 for 2 days during their shipment to the laboratory, after which they were preserved for longer term storage (~1 month) with acid-permanganate.

lake samples, low in turbidity and color, were collected in cleaned polyethylene and FEP teflon containers. Samples were immediately acidified and metal additions were made to six of the samples (3 teflon, 3 polyethylene) just prior to analysis. Two samples taken in polyethylene and one in teflon remained acidified and unspiked. All time zero analyses were completed within 8 h after sample collection, except for Mn which was completed within 24 h. In calculating the mean and standard deviation no distinction was made between teflon and polyethylene containers, since concentration differences for the two container types were generally equal within experimental error. Therefore, at each time interval mean spiked lake water values are based on six samples and mean unspiked values are based on three samples. All samples were analyzed using the furnace method. Results indicate that little if any change occurred over the 40- and 106-day mean intervals of measurement except in the case of Cr(VI) and As(V), where a concentration decrease in the spiked concentrations is readily apparent. These data may be compared with previous findings (Strumpler 1973, Rattonetti 1976). Samples for Hg were usually stored acidified 2-3 days in polyethylene or teflon containers before H_2SO_4 and $KMnO_4$ reagents were added to permanently stabilize the samples before analysis. Therefore, similar stability experiments were conducted with six Hg(II) spiked Lake Superior water samples (3 teflon, 3 polyethylene) to determine possible short-term losses under these conditions. Approximately 80% of the nominal spike remains in solution after a 5- to 6-day storage period (Table 4). Although many reports show that a loss of Hg from distilled water solutions occurs under a variety of conditions (Newton and Roscoe 1974, Feldman 1974, Lo and Wai 1975, Christmann and Ingle 1976, Coyne and Collins 1972), some recent works for natural waters (Das and Van der Sloot 1976, Robertson 1976) suggest that similar or higher percentages of both HG(II) and CH_3Hg remain in solution at $pH < 2$ for storage periods of several days in polyethylene. Because of the many apparent conflicting studies on this subject, more definitive work is needed on sample storage of Hg and other elements in various types of natural waters. The sample stability data given here is meant to serve only as a guide for interpretation of these data.

Overall Analytical Reproducibility

Taking several replicate water samples at a particular location and time and subjecting them to the analytical procedure was particularly useful in delineating the quality of the data with respect to a particular application. The mean of the relative standard deviations (RSD) for three to five unfiltered acidified samples per station was calculated for elements in which nearly 100% frequency of detection was obtained (Table 5). The mean and range of concentrations are given in Table 7. Although the mean RSD value for each element is quite acceptable for these low concentration ranges, some may be slightly higher than normal analytical reproducibility for determining the mean element concentration for a single sample. Pb reproducibility is the poorest since concentrations were nearest the analytical detection limit.

Sample Analysis

Previous studies have considered analytical accuracy for the determination of some elements in certain natural waters by flameless atomic absorption methods (Robertson 1976, Poldoski and Glass 1976, Poldoski 1977, Poldoski and Glass 1977, Poldoski and Glass 1978). Table 2 summarizes the results of percent recovery calculations based on the mean for samples from approximately 48 different stations. A sample from each station was spiked with known amounts of the element. The percent recovery was defined as 100 times the absorbance change per nominal unit concentration change for the acidified sample divided by the absorbance change per nominal unit concentration change for acidified deionized distilled water; determinations were within a linear region of the standard curve. Only Cr and Pb mean recoveries were significantly below 100%.

Determining the total As concentration in water samples containing a high suspended clay concentration presented difficulties. From a separate study (Poldoski 1977), it was determined that a molecular spectral interference was present for this particular matrix but that it could be identified and substantially reduced or eliminated by adding hydrofluoric acid to the sample, using a narrow spectral bandpass, or subjecting the sample to the digestion procedure previously described. Results of applying this digestion procedure for several elements, including As, are given in Table 6. Samples were high in suspended solids, color or dissolved substances except for the Lake Superior sample from the water intake at the Environmental Research Laboratory-Duluth, which is a soft water typically low in natural organic content and suspended solids. Agreement between undigested and digested samples is generally within experimental

TABLE 5. Overall reproducibility of sampling, sample handling, and analysis for replicate water samples.

Element	Mean Relative Standard Deviation	Standard Deviation	Range	Number (location)
As	13	10	0.4-38	46
Cu	26	21	13-94	48
Fe	15	10	0.3-43	48
Mn	14	13	1.3-60	48
Pb	36	21	0-75	44

absorption, the lower concentration observed for the undigested Ontonagon sample was probably due to suspended solids reducing the atomization or nebulization efficiency during aspiration.

Qualitative Results

Analytical results for Hg and Ni were generally qualitative in nature since the percentage of the total number of stations (45-48) with concentrations less than instrumental detection limits were 76 and 74, respectively. By averaging all values, including the analytical detection limits for those stations in which the metal was undetectable, the means and standard deviations were $<0.02 \pm 0.01$ μg/L for Hg and $<1.2 \pm 1.3$ μg/L for Ni. These values coincide with other recent works for natural waters (Das and Van der Sloot 1976, Robertson 1976, Poldoski and Glass 1977). More sensitive analytical methods would be desirable since extremely low concentrations of CH_3Hg in water are known to produce undesirable mercury residues in fish (Olson *et al.* 1975).

TABLE 6. Comparison of atomic absorption analytical results for undigested versus digested samples. Hydrofluoric acid pressure digestion procedure was employed.

	Concentration (μg/L)									
	Cu		Fe		Mn		Pb		As	
Sample (unfiltered)	Dig.	Undig.	Dig.	Undig.	Dig.	Undig.	Dig.	Undig.	Dig.	Undig.
Black River, 1-RB	2.2	2.5	520	480	31	33	0.7	0.5	1.1	1.2
Ontonagon River, 2-RB	11.8	10.7	5500	3550	111	77	4.8	4.6	2.3	13.2
Saginaw River, 18-RE	4.7	4.6	650	700	79	80	5.3	4.9	4.6	4.9
Tahquamenon River, 25-RA	0.5	0.7	1160	1230	33	35	—	—	1.7	1.3
Lake Superior, ERL-D	1.3	1.3	—	—	—	—	0.2	0.2	1.1	1.0

TABLE 7. Mean trace element concentrations for all sampling locations of Lakes Superior and Huron and incoming streams. Superscripts indicate percentage of locations classified as less than detection (less than values were generally averaged in calculating the mean).

Element	Mean Total Concentration (μg/L)	Range (μg/L)	Number (locations)
As	1.0 ± 0.7	0.6-5.4	47
Cr	$0.9^{a} \pm 1.8$	<0.3-11	48
Cu	2.0 ± 1.8	0.5-9.1	48
Fe	236 ± 819	3.9-5500	48
Mn	14 ± 34	0.3-185	48
Pb	$0.7^{b} \pm 0.8$	<0.2-4.5	48

[a]42.
[b]6.

error for all five elements except for the Ontonagon River sample, which unlike the other samples contained a high concentration of suspended clay. This case exemplifies the degree of spectral interference which can be observed for As, up to fivefold or possibly more. For Pb and Cu, agreement with and without digestion was within experimental error; however, for Fe and Mn significant discrepancies are apparent. Since Fe and Mn were the only elements determined by direct aspiration flame atomic

Semiquantitative and Quantitative Results

Mean trace element concentrations for unfiltered samples at all sampling locations are given in Table 7. The frequency of detection as a function of station was 100% for all elements except for Pb and Cr in which the values were 94% and 58%, respectively. Table 8 gives mean concentrations as a function of distance from the shore area for both Lakes. Concentrations tend to be lowest for the location furthest from shore. Highest concentrations are in the river mouths, however, mean concentrations are still relatively low. Results represent total element concentrations, thus these data may be compared to trace element concentrations found for other studies (Chau *et al.* 1970, Copeland and Ayers 1972, Bramen and

TABLE 8. Mean trace element concentrations (μg/L) in unfiltered samples from various near-shore mid-depth locations of Lakes Superior and Huron. Superscripts indicate percentage of locations classified as less than detection.

	As	Cr	Cu	Fe	Mn	Pb
Lakes (2500 meters off-shore) 23 locations	0.8 ±0.1	0.4[a] ±0.2	1.6 ±0.6	17 ±12	0.9 ±0.4	0.5[d] ±0.2
Lakes (100 meters off-shore) 13 locations	0.8 ±0.1	0.4[b] ±0.2	1.2 ±0.5	34 ±32	1.8 ±1.5	0.4[e] ±0.2
Rivers (Mouth 12 locations	1.4 ±1.3	2.4[c] ±3.2	3.6 ±3.1	874 ±1507	53 ±52	1.4 ±1.5

[a] 52
[b] 62
[c] 25
[d] 9
[e] 8

Forebach 1973, Poldoski and Glass 1977), although direct comparisons may not always be possible due to differences in the method employed. However, one study should be particularly noted. In the determination of Pb, Patterson and Settle (1976) have provided data which strongly contrasts to most other known data on Pb in natural freshwaters. For lakes in the high Sierra mountain ranges of the western United States, they obtained values (0.014 μg/L), far below those of Bradford *et al.* (1968) for the same area (0.3 μg/L). Patterson and Settle attributed this difference to contamination during sample collection in Bradford's study. In certain types of sampling programs involving trace elements, it is sometimes near impossible to know with absolute certainty whether an inherent contamination error was operative such as during shipboard sampling procedures (Rice and Jasinski 1976). In our study, values (unfiltered samples) for Pb at 2500 m offshore averaged 0.4-0.6 μg/L for both lakes. These values compare very favorably to baseline values obtained for a study of low turbidity stream waters in the northern Minnesota wilderness (Poldoski and Glass 1977) where significant contamination problems in sampling were greatly minimized. Further study is needed to determine if these apparent differences between the high Sierra lakes and the upper Great Lakes area are a natural occurrence.

Some of the highest concentrations observed in our study are listed in Table 9. Results from four locations are presented in which concentrations

TABLE 9. Locations where trace element concentrations[a] (μg/L) in unfiltered samples were elevated more than one standard deviation above the overall mean for lakes and streams.

	As	Cr	Cu	Fe	Mn	Ni	Pb
Lake Superior							
Ontonagon River, 2R	—	11 ±2 (5)[b]	9.1 ±0.2 (35)	5500[c] (2)	111[c]	5.1 ±2.0 (<26)	4.0 ±0.3 (<5)
Carp River, 21R	—	3.3 ±0.4 (<83)	8.2 ±0.4 (21)	—	185 ±10 (40)	—	2.2 ±0.6 (<7)
Lake Huron							
Tawas River, 17R	—	—	—	—	61 ±2 (37)	4.0 ±0.3 (82)	—
Saginaw River, 18R	5.4 ±0.3 (82)	6.5 ±3.9	4.7 ±0.1 (<42)	—	76 ±0.7 (6)	8.0 ±0.3	4.5 ±0.1

[a] Mean of 3-5 samples per station.
[b] Indicates percent dissolved element (0.1 μm): 100X (concentration in filtered sample)/(concentration in unfiltered sample).
[c] Based on one sample.

tended to be most elevated. For Lake Superior, the incoming Ontonogan River shows somewhat elevated values for Cr, Cu, Mn, Ni, Pb, and especially Fe. The Carp River had noticeably elevated Cr, Cu, Mn, and Pb concentrations although none tremendously high. For two Lake Huron streams, the Tawas River contained slightly elevated Mn and Ni concentrations whereas the Saginaw River displayed distinctly elevated concentrations of As, Cr, Cu, Mn, Ni, and Pb. Of these cases, only Ni in the Tawas River and As in the Saginaw River displayed "dissolved" values which were greater than 50% of the total concentration; however, the average for As for all stations was about 90% "dissolved". Most of the elevated values for both filtered and unfiltered samples were well above each of the corresponding ambient offshore lake station values and none of the lake stations exhibited similar high concentrations for any of these elements.

As a final consideration, the question of possible concentration differences between Lakes Superior and Huron is addressed in Table 10. The mean element concentrations (unfiltered) for rivermouths and all locations that were approximately 2500 m offshore are given. Except for Mn, concentrations appear nearly identical for the two lakes. More sampling as a function of time and location is required to discern any statistically meaningful overall differences.

TABLE 10. Mean total trace element concentrations (μg/L) in near-shore waters and river mouths for Lakes Superior and Huron.

	Near-Shore (2500 m)		River Mouth	
Element	Superior	Huron	Superior	Huron
As	0.8 ± 0.1	0.8 ± 0.1	1.0 ± 0.1	2.2 ± 2.2
Cu	1.5 ± 0.4	1.6 ± 0.8	4.5 ± 3.2	1.8 ± 2.0
Fe	16 ± 15	18 ± 5	1142 ± 1815	339 ± 255
Pb	0.4 ± 0.2	0.6 ± 0.2	1.2 ± 1.3	1.7 ± 1.9
Mn	0.6 ± 0.2	1.3 ± 0.2	57 ± 62	45 ± 32

SUMMARY

These studies clearly indicate that blank samples should be obtained at various steps in sampling and sample handling procedures to produce internal checks on the likelihood of sample contamination.

Graphite furnace atomic absorption spectrometry procedures demonstrated adequate sensitivity to provide quantitative determinations of As, Cu, Fe, and Mn. However, more sensitive procedures are required for Hg, Pb, Ni, and Cr determinations, particularly for filtered samples.

Although a molecular spectral interference in the determination of As is possible when high concentrations of suspended clays are present, such concentrations were uncharacteristic of all lake stations and most rivers sampled. Application of proper analytical procedures can circumvent this problem.

Sample stability experiments indicated that measurable fractions of Cr(VI) and As(V) concentrations may possibly be lost from spiked Lake Superior samples when stored up to 15 weeks under the specified conditions and small fractions of Hg(II) may disappear from spiked solutions within 1 week.

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REFERENCES

Bradford, G. R., Bair, F. L., and Hunsaker, V. 1968. Trace and major element content of 170 high Sierra Lakes in California. *Limnol. Oceanogr.*, 13:526-530.

Bramen, R. S., and Forebach, C. C. 1973. Methylated forms of arsenic in the environment. *Science*, 182:1247-1249.

Bothner, M. H., and Robertson, D. E. 1975. Mercury contamination of seawater samples stored in polyethylene containers. *Anal. Chem.*, 47:592-595.

Chau, Y. K., Chawla, V. K., Nicholson, H. F., and Vollenweider, R. A. 1970. Distribution of trace elements and chlorophyll-a in Lake Ontario. *Proc. 13th Conf. Great Lakes Res. Internat. Assoc. Great Lakes Res.*, pp. 659-672.

_____ and Saitoh, H. 1973. Mercury in the International Great Lakes. *Proc. 16th Conf. Great Lakes Res., Internat. Assoc. Great Lakes Res.*, pp. 221-232.

Christmann, D. R., and Ingle, J. D. 1976. Problems with sub-P.P.B. mercury determinations: preservation of standards and prevention of water mist interferences. *Anal. Chim. Acta.*, 86:53-62.

Copeland, R. A., and Ayers, J. C. 1972. Trace element distributions in water, sediment, phytoplankton, zooplankton and benthos of Lake Michigan: A baseline study with calculations of concentration factors and buildup of radioisotopes in the food web. ERG Special Report No. 1, Environmental Research Group Inc.

Coyne, R. V., and Collins, J. A. 1972. Loss of mercury from water during storage. *Anal. Chem.*, 44:1093-1096.

Das, H. A., and van der Sloot, H. A. 1976. Sampling problems and the determination of mercury in surface water, seawater and air. U.S. National Bureau of Standards, Special Publication 422, Vol. II, Accuracy in trace analysis: Sampling, sample handling and analysis, *Proc. of 7th IMR symposium*, pp. 669-699.

Feldman, C. 1974. Preservation of dilute mercury solutions. *Anal. Chem.*, 46:99-102.

Glass, G. E., and Poldoski, J. E. 1976. Interstitial water components and exchange across the water sediment interface of Western Lake Superior. *Verh. Internat. Verein. Limnol.*, 19:405-420.

Hatch, W. R., and Ott, W. L. 1968. Determination of submicrogram quantities of mercury by atomic absorption spectroscopy. *Anal. Chem.*, 40:2085-2087.

Kopp, J. F., Longbottom, M. C., and Labring, L. B. 1972. Cold vapor method for determining mercury. *J. Amer. Water Works Assoc.*, 64:20-25.

Lo, J. M., and Wai, C. M. 1975. Mercury loss from water during storage: Mechanisms and prevention. *Anal. Chem.*, 47;1869-1870.

Newton, D. W., and Roscoe, E. 1974. Loss of mercury (II) from solution. *J. Environ. Quality*, 3:20-23.

Olson, G. F., Mount, D. I., Snarski, V. M., and Thorslund, T. W. 1975. Mercury residues in Fathead Minnows, *Pimephales promelas Rafinesque*, chronically exposed to methylmercury in water. *Bull. Environ. Contam. Toxicol.*, 14:129-134.

Patterson, C. C., and Settle, D. M. 1976. The reduction of orders of magnitude errors in lead analyses of biological materials and natural waters by evaluating and controlling the extent and sources of industrial lead contamination introduced during sample collecting and analysis. U.S. National Bureau of Standards, Special Publication 422, Vol. I, Accuracy in trace analysis: Sampling, sample handling and analysis. *Proc. of 7th IMR Symposium*, pp. 321-351.

Perkin Elmer Corp. 1971. Analytical methods for atomic absorption spectrophotometry. Norwalk, Conn.

Poldoski, J. E. 1977. Molecular spectral interference in the determination of arsenic by furnace atomic absorption. *At. Absorption Newslett.*, 16:70-73.

_____ and Glass, G. E. 1976. Methodological considerations in Western Lake Superior water-sediment exchange studies of some trace elements. U.S. National Bureau of Standards, Special Publication 422, Vol. II, Accuracy in trace analysis: Sampling, sample handling, and analysis. *Proc. of the 7th IMR Symposium*, pp. 1073-1088.

_____ and _____. 1977. Considerations of trace element chemistry for streams in the Minnesota-Ontario border area. *Proc. International Conf. Heavy Metals in the Environment, Toronto, Ontario, Canada, Oct. 27-31, 1975*, pp. 901-922.

_____ and _____. 1978. Anodic stripping Voltammetry at a mercury film electrode: aspects of determining baseline concentrations of cadmium, lead and copper in selected natural waters. *Anal. Chim. Acta.*, in press.

Rattonetti, A. 1976. Stability of metal ions in aqueous environmental samples. U. S. National Bureau of Standards, Special Publication 422, Vol. I, Accuracy in trace analysis: Sampling, sample handling and analysis. *Proc. of 7th IMR Symposium*, pp. 669-699.

Rice, G. K. and Jasinski, R. J. 1976. Monitoring dissolved copper in seawater by means of ion-selective electrode. U.S. National Bureau of Standards, Special Publication 422, Vol. II, Accuracy in trace analysis: Sampling, sample handling, and analysis. *Proc. of 7th IMR Symposium*, pp. 899-915.

Robertson, D. E. 1976. Analytical chemistry of natural waters. U.S. National Bureau of Standards, Special Publication 422, Vol. II, Accuracy in trace analysis: Sampling, sample handling, and analysis. *Proc. of 7th IMR Symposium*, pp. 805-836.

Strumpler, A. W. 1973. Absorption characteristics of silver, lead, cadmium, zinc and nickel on borosilcate glass, polyethylene and polypropylene container surfaces. *Anal. Chem.*, 45:2251-2254.

U.S.-Canadian International Joint Commission. 1977. Upper Lakes Reference Group Report. The waters of Lake Huron and Lake Superior, Vol. II and III.

Wagner, D. M., Lemire, R. S., and Anderson, D. W. 1976. Water quality studies of sixteen Minnesota rivers tributary to Lake Superior. *J. Great Lakes Res.*, 20:111-123.

Weiler, R. R., and Chawla, V. K. 1969. Dissolved mineral water quality of Great Lakes waters. *Proc. 12th Conf. Great Lakes Res., Internat. Assoc. Great Lakes Res.*, pp. 801-818.